

EAST Search History

| Re f # | Hits | Search Query | DBs | Defau lt Opera tor | Plur als | Time Stamp |
|-----------|------|-------------------------|---|-----------------------------|-------------|---------------------|
| L1 | 219 | (558/462).CCLS. | US-PGP UB; USPAT; USOCR ; EPO; JPO; DERWE NT; IBM_T DB | OR | OFF | 2007/08/02 14:46 |
| L2 | 10 | L1 AND ISOMERIZATION | US-PGP UB; USPAT; USOCR ; EPO; JPO; DERWE NT; IBM_T DB | OR | ON | 2007/08/02 14:48 |

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FILE 'HOME' ENTERED AT 14:49:14 ON 02 AUG 2007

=> EILE CAPLUS

EILE IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.
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"HELP COMMANDS" at an arrow prompt (=>).

=> FILE CAPLUS

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'CAPLUS' ENTERED AT 14:49:45 ON 02 AUG 2007

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FILE COVERS 1907 - 2 Aug 2007 VOL 147 ISS 6

FILE LAST UPDATED: 1 Aug 2007 (20070801/ED)

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<http://www.cas.org/infopolicy.html>

=> S CIS(L) PENTENENITRILE

224712 CIS

870 PENTENENITRILE

95 PENTENENITRILES

887 PENTENENITRILE

(PENTENENITRILE OR PENTENENITRILES)

L1 90 CIS(L) PENTENENITRILE

=> L1 AND ISOMERIZATION

L1 IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system.
For a list of commands available to you in the current file, enter
"HELP COMMANDS" at an arrow prompt (=>).

10553916>

08/02/2007

=> S L1 AND ISOMERIZATION

100114 ISOMERIZATION

3095 ISOMERIZATIONS

100784 ISOMERIZATION

(ISOMERIZATION OR ISOMERIZATIONS)

L2 30 L1 AND ISOMERIZATION

=> S L2 AND TRANS (L) PENTENENITRILE

266594 TRANS

6 TRANSES

266598 TRANS

(TRANS OR TRANSES)

870 PENTENENITRILE

95 PENTENENITRILES

887 PENTENENITRILE

(PENTENENITRILE OR PENTENENITRILES)

97 TRANS (L) PENTENENITRILE

L3 25 L2 AND TRANS (L) PENTENENITRILE

=> D IBIB ABS HITSTR TOT

10553916>

08/02/2007

L3 ANSWER 1 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2007:184030 CAPLUS
 DOCUMENT NUMBER: 146:441892
 TITLE: Nickel Complexes Involved in the Isomerization of 2-Methyl-3-butenenitrile
 AUTHOR(S): Acosta-Ramirez, Alberto; Flores-Gaspar, Areli; Munoz-Hernandez, Miguel; Arevalo, Alma; Jones, William
 CORPORATE SOURCE: D. J. Garcia, Juvenino J. Facultad de Quimica, Universidad Nacional Autonoma de Mexico, Mexico City, 04510, Mex.
 SOURCE: Organometallica (2007), 26(7), 1712-1720
 CODEN: ORGN7; ISSN: 0276-7333
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 146:441892
 AB The Ni(O) fragment [(P-P)Ni], where (P-P) = dtppe (1,2-bis(dicyclohexylphosphino)ethane) or dtpbe (1,2-bis(di-tert-butylphosphino)ethane), reacts with the cyano-olefins involved in the isomerization process of 2-methyl-3-butenenitrile (2M3BN), producing the corresponding complex [(P-P)Ni(η^2 -C,C-cyano-olefin)]. In the case of 2M3BN and 3-pentenitrile (3PN), the π -methylallyl metal complex was observed in solution. All of the intermediates in the catalytic cycle were detected and characterized by heteronuclear NMR spectroscopy; some of these were also characterized by single-crystal x-ray diffraction studies. The initial catalytic behavior of this system for the isomerization of 2M3BN was studied also.
 REFERENCE COUNT: 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 2 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2006:452705 CAPLUS
 DOCUMENT NUMBER: 145:62468
 TITLE: Identification, by selective poisoning, of active sites on Ni/Al₂O₃ for hydrogenation and isomerization of cis-2-pentenitrile
 AUTHOR(S): Canning, Arren S.; Jackson, S. David; Mitchell, Scott
 CORPORATE SOURCE: WestCHEM, Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK
 SOURCE: Catalysis Today (2006), 114(4), 372-376
 CODEN: CATTEA; ISSN: 0920-5861
 PUBLISHER: Elsevier B.V.
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The hydrogenation of cis-2-pentenitrile (C2PN) has been studied over Ni/alumina. Hydrogenation to n-pentenitrile (PN) and subsequent isomerization to trans-2-pentenitrile (T2PN) and trans-3-pentenitrile (T3PN) was observed. 1-Pentanamine (PA) was also detected in the initial stages of the catalyst life. Use of selective poisoning of metal sites with carbon monoxide and acid sites with ammonia revealed that hydrogenation was a function of the metal, while isomerization was solely a function of the support. 1-Pentanamine was produced by the support but the site was rapidly deactivated due to carbon deposition.
 REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 3 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2005:729624 CAPLUS
 DOCUMENT NUMBER: 143:195587
 TITLE: Catalytic isomerization of cis-2-pentenitrile into 3-pentenitriles in a reactive distillation column
 INVENTOR(S): Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael; Haderlein, Gerd; Baumann, Robert; Luyken, Hermann
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 23 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------------|------------|
| WO 2005073177 | A1 | 20050811 | WO 2005-EP782 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TG, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004716 | A1 | 20050818 | DE 2004-102004004716 | 20040129 |
| CA 2553779 | A1 | 20050811 | CA 2005-2553779 | 20050127 |
| EP 1713765 | A1 | 20061025 | EP 2005-701206 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914164 | A | 20070214 | CN 2005-80003649 | 20050127 |
| BR 2005007125 | A | 20070619 | BR 2005-7125 | 20050127 |
| JP 2007519676 | T | 20070719 | JP 2006-550102 | 20050127 |
| IN 2006C03122 | A | 20070608 | IN 2006-CN3122 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004716A | 20040129 |
| | | | WO 2005-EP782 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195587
 AB A method for the isomerization of cis-2-pentenitrile in an educt flow is described into 3-pentenitriles in which the isomerization is carried out on a heterogeneous catalyst in a distillation column, such that during the isomerization, the isomerization educt is enriched by distillation in relation to the isomerization product in the reaction column of the distillation column using a Group IIIA (e.g., alumina) or B oxide catalyst. An apparatus diagram is presented.
 REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 4 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2005:729623 CAPLUS
 DOCUMENT NUMBER: 143:195586
 TITLE: Catalytic homogeneous isomerization of cis-2-pentenitrile into 3-pentenitriles
 INVENTOR(S): Scheidel, Jens; Miller, Christian; Baumann, Robert; Jungkamp, Tim; Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann; Siegel, Wolfgang; Bassler, Peter
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 20 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------------|------------|
| WO 2005073176 | A1 | 20050811 | WO 2005-EP770 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TG, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004717 | A1 | 20050818 | DE 2004-102004004717 | 20040129 |
| CA 2553041 | A1 | 20050811 | CA 2005-2553041 | 20050127 |
| EP 1713764 | A1 | 20061025 | EP 2005-701200 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914165 | A | 20070214 | CN 2005-80003674 | 20050127 |
| BR 2005007195 | A | 20070626 | BR 2005-7195 | 20050127 |
| JP 2007519670 | T | 20070719 | JP 2006-550094 | 20050127 |
| US 2007515980 | A1 | 20070705 | US 2006-586481 | 20060720 |
| IN 2006C03132 | A | 20070608 | IN 2006-CN3132 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004717A | 20040129 |
| | | | WO 2005-EP770 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195586
 AB A method for the isomerization of cis-2-pentenitrile into trans-3-pentenitrile in an educt flow is described where the isomerization is performed using a dissolved catalyst (e.g., hexylamine).
 REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

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L3 ANSWER 5 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER:

2005:729618 CAPLUS

DOCUMENT NUMBER:

143:195581

TITLE:

Catalytic hydrocyanation method for producing 3-pentenitrile from hydrogen cyanide and 1,3-butadiene

INVENTOR(S):

Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael; Haderlein, Gerd; Baumann, Robert; Luyken, Hermann

PATENT ASSIGNEE(S):

BASF Aktiengesellschaft, Germany

SOURCE:

PCT Int. Appl., 55 pp.

CODEN: PIXXD2

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------------|------------|
| WO 2005073171 | A1 | 20050811 | WO 2005-EP774 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SE, SZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004720 | A1 | 20050818 | DE 2004-102004004720 | 20040129 |
| CA 2552860 | A1 | 20050811 | CA 2005-2552860 | 20050127 |
| EP 1716104 | A1 | 20061102 | EP 2005-701203 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914154 | A | 20070214 | CN 2005-80003621 | 20050127 |
| BR 2005006587 | A | 20070502 | BR 2005-6587 | 20050127 |
| JP 2007519672 | T | 20070719 | JP 2006-550097 | 20050127 |
| IN 2006CN03123 | A | 20070608 | IN 2006-CN3123 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004720A | 20040129 |
| | | | WO 2005-EP774 | W 20050127 |

OTHER SOURCE(S):

CASREACT 143:195581

AB A method is described for producing 3-pentenitrile comprising: (a) 1,3-butadiene is reacted with hydrogen cyanide over at least one catalyst to obtain a flow (1) containing 3-pentenitrile, 2-methyl-3-butenitrile, the catalyst, and 1,3-butadiene; (b) the flow (1) is distilled in a column to obtain a head product flow (2) rich in 1,3-butadiene, and a bottom product flow (3) that is poor in 1,3-butadiene and contains 3-pentenitrile, the catalyst, and 2-methyl-3-butenitrile; (c) the flow (3) is distilled in a column to obtain a head product flow (4) containing 1,3-butadiene, a flow (5)

L3 ANSWER 6 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER:

2004:927160 CAPLUS

DOCUMENT NUMBER:

141:379640

TITLE:

Method for the catalytic isomerization of cis-2-pentenitrile into trans-3-pentenitrile using alumina with a BET surface area of 250 m²/g

INVENTOR(S):

Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Flores, Miguel; Jungkamp, Tim; Luyken, Hermann; Scheidel, Jens; Siegel, Wolfgang; Kunsmann-Keitel, Dagmar Pascale

PATENT ASSIGNEE(S):

BASF Aktiengesellschaft, Germany

SOURCE:

PCT Int. Appl., 11 pp.

CODEN: PIXXD2

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| WO 2004094364 | A1 | 20041104 | WO 2004-EP4040 | 20040416 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
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| DE 10323803 | A1 | 20041111 | DE 2003-10323803 | 20030422 |
| CA 2522799 | A1 | 20041104 | CA 2004-2522799 | 20040416 |
| EP 1622862 | A1 | 20060208 | EP 2004-727882 | 20040416 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK | | | | |
| BR 2004009290 | A | 20060411 | BR 2004-9290 | 20040416 |
| CN 1777578 | A | 20060524 | CN 2004-80010823 | 20040416 |
| JP 2006524201 | T | 20061026 | JP 2006-505163 | 20040416 |
| US 2006194979 | A1 | 20060831 | US 2005-553916 | 20051020 |
| IN 2005CH03104 | A | 20070518 | IN 2005-CN3104 | 20051122 |
| PRIORITY APPLN. INFO.: | | | DE 2003-10323803 | A 20030422 |
| | | | WO 2004-EP4040 | W 20040416 |

OTHER SOURCE(S):

CASREACT 141:379640

AB A method is described for the isomerization of 2-pentenitrile into trans-3-pentenitrile in the presence of an alumina catalyst which has a BET surface of the alumina is 250 m²/g.

REFERENCE COUNT:

2

THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE

FORMAT

L3 ANSWER 5 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

ACCESSION NUMBER:

2004:778550 CAPLUS

DOCUMENT NUMBER:

141:279441

TITLE:

Procedure for the catalytic isomerization of 2-methyl-3-butenitrile into linear pentenenitriles

INVENTOR(S):

Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Flores, Miguel; Jungkamp, Tim; Luyken, Hermann; Scheidel, Jens; Siegel, Wolfgang; Kunsmann-Keitel, Dagmar Pascale

PATENT ASSIGNEE(S):

BASF A.-G., Germany

SOURCE:

Ger. Offen., 9 pp.

CODEN: GWXXBX

DOCUMENT TYPE:

Patent

LANGUAGE:

German

FAMILY ACC. NUM. COUNT:

1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| DE 10311119 | A1 | 20040923 | DE 2003-10311119 | 20030312 |
| WO 2004080949 | A1 | 20040923 | WO 2004-EP1800 | 20040224 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SE, SZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| PRIORITY APPLN. INFO.: | | | DE 2003-10311119 | A 20030312 |

OTHER SOURCE(S):

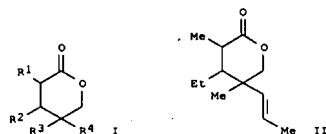
CASREACT 141:279441

AB A process is described for the isomerization of 2-methyl-3-butenitrile into linear pentenenitriles in the presence of a catalyst system comprising: (A) elemental Ni; (B) a trivalent phosphorus-containing compound ligand; and (C) a Lewis acid. Linear pentenenitriles are removed from the reaction mixture during the isomerization.

L3 ANSWER 8 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2004:292019 CAPLUS
 DOCUMENT NUMBER: 140:321236
 TITLE: Preparation of valerolactone compounds and perfume composition
 INVENTOR(S): Tanaka, Sakuya; Fukuda, Kazuyuki; Asada, Takahiro
 PATENT ASSIGNEE(S): Kao Corporation, Japan
 SOURCE: PCT Int. Appl., 65 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: Japanese
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------|------------|
| WO 2004029033 | A1 | 20040408 | WO 2003-JP12341 | 20030926 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MY, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| JP 2004161746 | A | 20040610 | JP 2003-323125 | 20030916 |
| AU 2003272896 | A1 | 20040419 | AU 2003-272896 | 20030926 |
| EP 1555261 | A1 | 20050720 | EP 2003-753957 | 20030926 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK | | | | |
| CN 1684949 | A | 20051019 | CN 2003-823085 | 20030926 |
| US 2006258559 | A1 | 20061116 | US 2005-529290 | 20050325 |
| PRIORITY APPLN. INFO.: | | | JP 2002-282675 | A 20020927 |
| | | | JP 2002-308952 | A 20021023 |
| | | | JP 2003-323125 | A 20030916 |
| | | | WO 2003-JP12341 | W 20030926 |

OTHER SOURCE(S): MARPAT 140:321236
 GI



L3 ANSWER 9 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2004:234771 CAPLUS
 DOCUMENT NUMBER: 141:39904
 TITLE: Hydrogenation of cis-2-pentenitrile over Ni/Al2O3 catalyst: coking, deactivation and reaction studies
 AUTHOR(S): Canning, Arran S.; Jackson, S. David
 CORPORATE SOURCE: Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK
 SOURCE: Preprints - American Chemical Society, Division of Petroleum Chemistry (2004), 49(1), 47-49
 CODEN: ACPCAT; ISSN: 0569-3799
 PUBLISHER: American Chemical Society, Division of Petroleum Chemistry
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 141:39904
 AB This paper investigates the heterogeneous gas-phase hydrogenation of multifunctional C-5 alkenes, in particular cis-2-pentenitrile over a Ni/Al2O3 catalyst, and examines the effect of carbon formation, the role of carbon and the deactivation for pentenenitrile hydrogenation in the gas-phase. There appears to be two phases of reaction and deactivation. In the first stage, the catalyst is 100% selective towards valeronitrile, but the catalyst deactivates rapidly depositing carbon on the surface. In the second phase, isomerization of the reactant is observed and the overall deactivation rate is decreased. The two stages of deactivation are a result of the presence of at least two active sites with differing activity.
 REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 8 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

AB Disclosed are a valerolactone compound represented by the formula (I) (wherein R1 and R2 each independently represents hydrogen, Me, or ethyl; R3 represents hydrogen or methyl; and R4 represents Pr, 1-propenyl, or phenyl; provided that not both of R1 and R2 are hydrogen), in particular, the valerolactone compound represented by the formula (II), and a process for producing that compound, and a perfume composition containing any of the valerolactone compds. Comps. I are useful as perfume or flavor compns. for household products, cosmetics, public health products, beverages, and foods such as detergents, fabric softeners, shampoos, body cleansers, milk flavors, milk coffee, or perfumes. Thus, Michael addition reaction of 2-pentenitrile with di-Me methylmalonate in the presence of NaOMe in methanol at 130° for 7 h and reduction of the resulting di-Me 2-methyl-2-[(1-cyanomethyl)propyl]malonate by LiBH4 in THF at 30° for 3 h gave 3-(cyanomethyl)-2-methyl-2-hydroxymethyl-1-pentanol which underwent hydrolysis in aqueous NaOH solution at 97° for 2.5 h and acidification with 6 N aqueous HCl solution to give 4-ethyl-5-(hydroxymethyl)-5-methyl-tetrahydropyran-2-one (III). Oxidation of III by pyridinium dichromate in CH2Cl2 at room temperature for 17 h and Wittig reaction of the resulting 4-ethyl-5-formyl-5-methyl-tetrahydropyran-2-one with ethyltriphenylphosphonium bromide using PPh4 in hexane/THF gave 4-ethyl-5-methyl-5-(cis-1-propenyl)-tetrahydropyran-2-one which underwent cis-trans isomerization in the presence of thiophenol and 2,2'-bisazobutyronitrile at 80° for 2 h to give 4-ethyl-5-methyl-5-(trans-1-propenyl)-tetrahydropyran-2-one.

L3 ANSWER 10 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2003:737717 CAPLUS
 DOCUMENT NUMBER: 139:262467
 TITLE: Phosphonite ligands and their use in hydrocyanation
 INVENTOR(S): Lenges, Christian P.; Lu, Helen S. M.; Ritter, Joachim
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA
 SOURCE: PCT Int. Appl., 25 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| WO 2003076394 | A1 | 20030918 | WO 2003-US7033 | 20030307 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| US 2003195371 | A1 | 20031016 | US 2002-93655 | 20020307 |
| US 6660877 | B2 | 20031209 | | |
| TW 266650 | B | 20061121 | TW 2002-91138062 | 20021231 |
| AU 2003218000 | A1 | 20030922 | AU 2003-218000 | 20030307 |
| US 2003195372 | A1 | 20031016 | US 2003-454074 | 20030604 |
| US 6737539 | B2 | 20040518 | | |
| US 2003212288 | A1 | 20031113 | US 2003-454024 | 20030604 |
| US 6846945 | B2 | 20050125 | | |
| PRIORITY APPLN. INFO.: | | | US 2002-93655 | A 20020307 |
| | | | WO 2003-US7033 | W 20030307 |

OTHER SOURCE(S): MARPAT 139:262467
 AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter. Thus, trans-3-pentenitrile was reacted in the presence of bis(1,5-cyclooctadiene) nickel, phosphonite bidentate ligand, and zinc dichloride to give an adiponitrile.
 REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE
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08/02/2007

L3 ANSWER 11 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:319912 CAPLUS
 DOCUMENT NUMBER: 138:321395
 TITLE: Phosphonites, use thereof as ligand in transition metal complexes and method for production of nitriles
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang; Molnar, Ferenc BASF Aktiengesellschaft, Germany PCT Int. Appl., 32 pp.
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 32 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| WO 2003013509 | A1 | 20030424 | WO 2002-EP11107 | 20021004 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 10150281 | A1 | 20030430 | DE 2001-10150281 | 20011012 |
| DE 10207165 | A1 | 20030821 | DE 2002-10207165 | 20020220 |
| CA 2464710 | A1 | 20030424 | CA 2002-2464710 | 20021004 |
| AU 2002362815 | A1 | 20030428 | AU 2002-362815 | 20021004 |
| EP 1438317 | A1 | 20040721 | EP 2002-801308 | 20021004 |
| EP 1438317 | B1 | 20060621 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002012965 | A | 20041013 | BR 2002-12965 | 20021004 |
| JP 2005050630 | T | 20050224 | JP 2003-536248 | 20021004 |
| CN 1639176 | A | 20050713 | CN 2002-819907 | 20021004 |
| AT 330962 | T | 20060715 | AT 2002-801308 | 20021004 |
| US 2005090678 | A1 | 20050428 | US 2004-491918 | 20040408 |
| US 7067685 | B2 | 20060627 | | |
| IN 2004CN01004 | A | 20060203 | IN 2004-CN1004 | 20040511 |
| PRIORITY APPL. INFO.: | | | DE 2001-10150281 | A 20011012 |
| | | | DE 2002-10207165 | A 20020220 |
| | | | WO 2002-EP11107 | W 20021004 |

OTHER SOURCE(S): CASREACT 138:321395; MARPAT 138:321395
 GI

L3 ANSWER 12 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:93132 CAPLUS
 DOCUMENT NUMBER: 138:137726
 TITLE: Isomerization and hydrocyanation of monolefinic C5-mononitriles in the presence of Ni(0)-phosphite/phosphonite catalysts
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang BASF AG, Germany Ger. Offen., 18 pp.
 PATENT ASSIGNEE(S): BASF AG, Germany
 SOURCE: Ger. Offen., 18 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| DE 10136488 | A1 | 20030206 | DE 2001-10136488 | 20010727 |
| TW 570839 | B | 20040111 | TW 2002-91115419 | 20020711 |
| CA 2454912 | A1 | 20030213 | CA 2002-2454912 | 20020716 |
| WO 2003011457 | A1 | 20030213 | WO 2002-EP7888 | 20020716 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2002355640 | A1 | 20030217 | AU 2002-355640 | 20020716 |
| EP 1414567 | A1 | 20040506 | EP 2002-791454 | 20020716 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002011455 | A | 20040817 | BR 2002-11455 | 20020716 |
| CN 1535179 | A | 20041006 | CN 2002-814769 | 20020716 |
| JP 2004535929 | T | 20041202 | JP 2003-516681 | 20020716 |
| MX 2004PA00559 | A | 20040420 | MX 2004-PA559 | 20040119 |
| US 2004176622 | A1 | 20040909 | US 2004-484169 | 20040120 |
| IN 2004CN00391 | A | 20051223 | IN 2004-CN391 | 20040226 |
| PRIORITY APPL. INFO.: | | | DE 2001-10136488 | A 20010727 |
| | | | WO 2002-EP7888 | W 20020716 |

OTHER SOURCE(S): MARPAT 138:137726
 AB Monolefinic C5-mononitriles, e.g., 2-methyl-3-butenenitrile (readily available from hydrocyanation of 1,3-butadiene), was isomerized into a mixture of linear mononitrile, e.g., 3-pentenitrile (main) with improved selectivity in the presence of Ni(0) complexes with chelating bisphosphite or bisphosphonite ligands. The pentenenitrile isomers can be further hydrocyanated with HCN to the corresponding dinitriles, e.g., adiponitrile, with the same catalysts and ZnCl₂ promoter.

L3 ANSWER 11 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB The invention relates to phosphinites I and II (R1, R2, R3, R4, R5, R6, R7, R8, R9 = independently represent H, C1-8 alkyl or alkylene, or C1-8 alkoxy; R3 = H, Me; R4 = i-Pr, t-butyl; X = F, Cl or CF₃; n = 1, 2) useful as cocatalysts for nickel catalyzed preparation of nitriles. Thus, nickel(0)/phosphonite-catalyzed isomerization of 2-methyl-3-butenenitrile to give 3-pentenitrile and same catalyst mediated hydrocyanation of 3-pentenitrile to give adipodinitrile is described.
 REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 13 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2000:519220 CAPLUS
 DOCUMENT NUMBER: 133:266964
 TITLE: Cationic Unsymmetrical 1,4-Diazabutadiene Complexes of Platinum(II)
 AUTHOR(S): Albiets, Paul J., Jr.; Yang, Kaiyuan; Lachicotte, Rene
 CORPORATE SOURCE: J. Eisenberg, Richard Department of Chemistry, University of Rochester, Rochester, NY, 14627, USA
 SOURCE: Organometallica (2000); 19(18), 3543-3555 CODEN: ORGN07; ISSN: 0276-7333
 PUBLISHER: American Chemical Society
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The synthesis of the silyl-protected 1,4-diazabutadiene ligands glyoxalbis(2-(n-triisopropylsiloxyethyl)-6-methylphenyl)dimine (TIPS-6-MPD) and glyoxalbis(2-(n-triisopropylsiloxyethyl)-4-methylphenyl)dimine (TIPS-4-MPD) and their subsequent reactions with trans-Pt(SMe₂)₂(Me)Cl to generate the corresponding complexes (TIPS-6-MPD)Pt(Me)Cl (1a) and (TIPS-4-MPD)Pt(Me)Cl (1b) are described. Cationic complexes [(N,N-chelate)Pt(Me)(L)]BF₄ (L = solvent/olefin and N,N-chelate = TIPS-6-MPD and TIPS-4-MPD) were generated by the reaction of chloro Me complexes 1a and 1b with AgBF₄ in the presence of L. Various exchange reactions were examined for [(TIPS-6-MPD)Pt(Me)(NCCH₃)]BF₄ (2a), in which the coordinated solvent reversibly exchanges with acrylonitrile, ethylene, fumaronitrile, cis-2-pentenitrile, benzonitrile, di-Me sulfide, and CO to generate the corresponding cationic complexes 3-9, resp. Kinetics expts. under pseudo-first-order conditions using 10⁻³, 20⁻³, and 30-fold excesses of benzonitrile demonstrate that 2a undergoes ligand exchange via an associative pathway with a binol. rate constant k₂ of (3.2 ± 2.0) × 10⁻⁴ M⁻¹ s⁻¹. Complex 2a initiates the polymerization of various electron-rich monomers. A detailed anal. of the reaction demonstrates that the initiation is cationic in nature. The structure of TIPS-6-MPD was determined by a single-crystal x-ray diffraction anal. The free ligand adopts an s-trans conformation with a planar N=C-C=N backbone.
 REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE
 FORMAT

L3 ANSWER 14 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1989:192269 CAPLUS
 DOCUMENT NUMBER: 110:192269
 TITLE: Preparation of 4-pentenitrile by isomerization of 3-pentenitrile
 INVENTOR(S): Burke, Patrick M.; Herron, Norman; Waller, Francis J.
 PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co., USA
 SOURCE: U.S., 5 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-------------|------|----------|-----------------|----------|
| US 4783546 | A | 19881108 | US 1987-57433 | 19870602 |
| JP 63310857 | A | 19881219 | JP 1988-130477 | 19880530 |
| CA 1331628 | C | 19940823 | CA 1988-568217 | 19880530 |
| EP 297302 | A1 | 19890104 | EP 1988-108770 | 19880531 |
| EP 297302 | B1 | 19921104 | | |

R: BE, DE, FR, GB, IT, LU, NL
 PRIORITY APPLN. INFO.: US 1987-57433 A 19870602

AB A process for preparing 4-pentenitrile (II) comprised isomerizing 3-pentenitrile (I) at approx. 50° to 150° at 0.1-50 atm with a heterogeneous catalyst selected from the group consisting of, acidic amorphous silica aluminates promoted with Pd in an oxidation state of 2+2 in an amount 0.1-4% by weight of the catalyst, acid Y-zeolites promoted with 0.1-4% Pd in an oxidation state of 2+2, and perfluorinated sulfonic acid ion-exchange polymers promoted with Pd or Pt in an oxidation state of 2+2. Crude II containing trans-II 93.6, cis-II 3.1, trans-2-pentenitrile I trans-(III) 1.4, cis-III 0.3, and I 1.5% was refluxed with Pd (2.84 weight %) promoted HY Zeolite catalyst to give, after 5 min, a mixture of cis-III 0.94, trans-III 1.18, I 10.90, trans-II 73.70, cis-II 13.28%.

L3 ANSWER 16 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1975:170121 CAPLUS
 DOCUMENT NUMBER: 82:170121
 TITLE: Selective isomerization of pentenenitriles
 INVENTOR(S): King, Charles M.
 PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
 SOURCE: U.S., 3 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-------------|------|----------|-----------------|----------|
| US 3852325 | A | 19741203 | US 1973-392515 | 19730829 |
| JP 50050319 | A | 19750506 | JP 1974-97610 | 19740827 |
| CA 1021350 | A1 | 19771122 | CA 1974-208036 | 19740827 |
| BE 819265 | A1 | 19750228 | BE 1974-147959 | 19740828 |
| NL 7411458 | A | 19750304 | NL 1974-11458 | 19740828 |
| DE 2441257 | A1 | 19750306 | DE 1974-2441257 | 19740828 |
| FR 2242376 | A1 | 19750328 | FR 1974-29408 | 19740828 |
| FR 2242376 | B1 | 19790105 | | |
| GB 1436511 | A | 19760519 | GB 1974-37607 | 19740828 |

PRIORITY APPLN. INFO.: US 1973-392515 A 19730829

AB A mixture containing 98% cis- (I) and 2% trans-2-pentenitrile (II) was heated to 140° for 1.5 hr in the presence of Ph3CBz to give a mixture containing 45.7% I and 53.7% II. Similar results were obtained with cis- and trans-3-pentenitrile.

L3 ANSWER 15 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1984:67539 CAPLUS
 DOCUMENT NUMBER: 100:67539
 TITLE: Mechanistic studies of nickel-catalyzed addition of deuterium cyanide and [13C]hydrogen cyanide to pentenenitriles
 AUTHOR(S): Druliner, J. D.
 CORPORATE SOURCE: Cent. Res. Dev. Dep., E. I. du Pont de Nemours and Co., Wilmington, DE, 19898, USA
 SOURCE: Organometallics (1984), 3(2), 205-8
 CODEN: ORGND7; ISSN: 0276-7333
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The addition of DCN and H13CN to pentenenitriles using a [(p-MeC6H4O)3P]4Ni (I) catalyst and AlCl3, ZnCl2, and BPh3 Lewis acids permits the assignment of major dinitrile product reaction paths. Patterns of D incorporation in recovered pentenenitriles are consistent with Ni hydride catalysis of both cis-trans and double-bond olefin isomerization reactions. 1H NMR anal. shows Ni-13CN bonding in complexes containing the L3NiH13CN (L = P-containing ligands) moiety but not in analogous complexes containing the L4Ni+H13CN moiety. H/D exchange occurs via o-metalation with [(p-MeOC6H4O)3P]4Ni but not with I.

L3 ANSWER 17 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1975:155417 CAPLUS
 DOCUMENT NUMBER: 82:155417
 TITLE: Selective cis/trans isomerization of 2-pentenitrile in a solution of pentenenitrile isomers
 INVENTOR(S): Druliner, Joe D.; King, Charles M.
 PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
 SOURCE: U.S., 4 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-------------|------|----------|-----------------|----------|
| US 3852327 | A | 19741203 | US 1973-392514 | 19730829 |
| JP 50050318 | A | 19750506 | JP 1974-97609 | 19740827 |
| BE 819264 | A1 | 19750228 | BE 1974-147958 | 19740828 |
| NL 7411457 | A | 19750304 | NL 1974-11457 | 19740828 |
| DE 2441253 | A1 | 19750306 | DE 1974-2441253 | 19740828 |
| FR 2242375 | A1 | 19750328 | FR 1974-29407 | 19740828 |
| FR 2242375 | B1 | 19790105 | | |
| GB 1447597 | A | 19760825 | GB 1974-37606 | 19740828 |

PRIORITY APPLN. INFO.: US 1973-392514 A 19730829

AB In a mixture of pentenenitriles, E- and Z-2-pentenitrile were brought closer to their equilibrium ratio by contacting the mixture with a Lewis acid-Lewis base catalyst composition. Thus, E-2-pentenitrile (I) was removed from a mixture containing mainly 3-pentenitrile by isomerizing I to the cis isomer and removing the more volatile cis isomer by fractional distillation. There was substantially no isomerization of 3-pentenitrile to E- and Z-2-pentenitrile.

L3 ANSWER 18 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1973:42868 CAPLUS
DOCUMENT NUMBER: 78:42868
TITLE: 3-Pentenitriles by catalytic isomerization of 2-methyl-3-butenitrile
INVENTOR(S): Drinkard, William Charles, Jr.
PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
SOURCE: Ger. Offen., 17 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 3
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|-------------|
| DE 2221113 | A | 19721116 | DE 1972-2221113 | 19720428 |
| US 3739011 | A | 19730612 | US 1971-139202 | 19710430 |
| CA 955957 | A1 | 19741008 | CA 1972-139458 | 19720411 |
| BE 782402 | A1 | 19720816 | BE 1972-116559 | 19720420 |
| NL 7205834 | A | 19721101 | NL 1972-5834 | 19720428 |
| FR 2136815 | A5 | 19721222 | FR 1972-15404 | 19720428 |
| GB 1379787 | A | 19750108 | GB 1972-19789 | 19720428 |
| IT 953871 | B | 19730810 | IT 1972-23748 | 19720429 |
| | | | US 1971-139202 | A 19710430 |
| | | | US 1969-876613 | A2 19691113 |

PRIORITY APPLN. INFO.:

AB trans-3-Pentenitrile (II) and its cis isomer (III) were prepared by isomerization of CH₂:CHCHMeCN (III) in the presence of a complex Ni(PR₃)_n (R = e.g., Ph or Et, n = 3 or 4) and an optional promoter, E.g. ZnCl₂, SnCl₂, NiCl₂, FeCl₂, or BPh₃, at 60-100°. Thus, heating 25 ml III with 1.5 g Ni(PPh₃)₃ and 0.26 g CoCl₂ for 22 hr at 100° gave 46.3% I and 1.0% II.

L3 ANSWER 19 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1972:404982 CAPLUS
DOCUMENT NUMBER: 77:4982
TITLE: 3-Pentenitrile by isomerization of 2-methyl-3-butenitrile
INVENTOR(S): Drinkard, William C., Jr.; Lindsey, Richard V., Jr.
PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
SOURCE: Ger. Offen., 16 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|-------------|
| DE 2149175 | A | 19720406 | DE 1971-2149175 | 19711001 |
| DE 2149175 | C2 | 19820304 | | |
| US 3496215 | A | 19700217 | US 1965-509432 | 19651123 |
| US 3536748 | A | 19701027 | US 1967-678171 | 19671026 |
| GB 1351694 | A | 19740501 | GB 1971-41937 | 19710908 |
| BE 772532 | A1 | 19720313 | BE 1971-108103 | 19710913 |
| CA 955956 | A1 | 19741008 | CA 1971-122952 | 19710915 |
| IT 945957 | B | 19730510 | IT 1971-29118 | 19710925 |
| NL 7113535 | A | 19720405 | NL 1971-13535 | 19711001 |
| FR 2110896 | A5 | 19720602 | FR 1971-35485 | 19711001 |
| US 3853948 | A | 19741210 | US 1972-286131 | 19720905 |
| | | | US 1970-77725 | A 19701002 |
| | | | US 1965-509432 | A2 19651123 |
| | | | US 1967-678171 | A2 19671026 |

PRIORITY APPLN. INFO.:

AB Cis-3-Pentenitrile (II) and its trans isomer (III) were prepared by isomerization of MeCH:CHMeCN (III) in the presence of Ni(PR₃)₃ (IV, R = Ph, Me, C₆H₅, or p-MeC₆H₄) and P(OR)₃ at 1:4-10 molar ratio. Thus, III containing 2.88% 3-pentenitrile was isomerized 23.5 hr at 130° in the presence of 1:4 (molar ratio) IV (R = Ph) and P(OPh)₃ to give 28.7% II and 0.16% I.

L3 ANSWER 20 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1971:31562 CAPLUS
DOCUMENT NUMBER: 74:31562
TITLE: Catalytic isomerization of 2-pentenitrile to 3-pentenitrile
INVENTOR(S): Hildebrand, Gary P.
PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
SOURCE: U.S., 2 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|------------|
| US 3526654 | A | 19700901 | US 1968-729883 | 19680517 |
| | | | US 1968-729883 | A 19680517 |

PRIORITY APPLN. INFO.:

AB The catalytic isomerization of cis-and trans -2-pentenitriles is carried out by passing the 2-pentenitrile over a solid state catalyst at 25-500° and 0.5-50 atm either in the liquid or vapor phase. Typical catalysts are solid state catalysts silica gel, alumina, or sodium calcium aluminosilicates, possessing either a large surface area either by fine division (20 mesh) or by high porosity. Any reactor capable of containing a liquid or gas medium is effective. The preferred reactor is an evaporator feeding the 2-pentenitrile to a column containing the catalyst. Four examples are given as typical isomerization reactions conditions and final sepns. This isomerization is useful in reducing a yield loss in the production of adiponitrile from 3-pentenitriles and 4-pentenitrile by means of catalytic hydrocyanation.

L3 ANSWER 21 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1970:78489 CAPLUS
DOCUMENT NUMBER: 72:78489
TITLE: Removal of trans-2-pentenitrile from 3- and 4-pentenitrile
INVENTOR(S): Downing, Roland G.; Fouty, Roger A.
PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
SOURCE: Ger. Offen., 18 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|------------|
| DE 1930267 | A | 19691218 | DE 1969-1930267 | 19690613 |
| DE 1930267 | B2 | 19730726 | | |
| DE 1930267 | C3 | 19740314 | | |
| US 3564040 | A | 19710216 | US 1968-737069 | 19680614 |
| BE 733162 | A | 19691117 | BE 1969-733162 | 19690516 |
| NL 6908981 | A | 19691216 | NL 1969-8981 | 19690612 |
| GB 1219995 | A | 19710120 | GB 1969-1219995 | 19690613 |
| | | | US 1968-737069 | A 19680614 |

PRIORITY APPLN. INFO.:

AB A process for the hydrocyanation of 3- or 4-pentenitrile to form adiponitrile is described in Brit. 1,104,140. Here the extent to which trans-2-pentenitrile in the charge causes catalyst poisoning in the process at 25-300° is reduced. The catalyst used is a Ni, Pd, or Co complex, such as a Ni(0)-tetrakis (triaryl phosphite), which catalyzes both the HCN addition and the isomerization of trans-2-pentenitrile to the cis isomer. In the continuous process, cis-2-pentenitrile is fractionally distilled from the reaction mixture so that the amount of 2-pentenitriles present is maintained at <5 mole %, based on all nitriles present in the reaction mixture

L3 ANSWER 22 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1969:470093 CAPLUS
 DOCUMENT NUMBER: 71:70093
 TITLE: Hydrides of nickel coordination compounds
 INVENTOR(S): Drinkard, William C., Jr.; Lindsey, Richard V., Jr.
 PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.
 SOURCE: Ger. Offen., 13 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|------|----------|-----------------|------------|
| DE 1808434 | C3 | 19730125 | DE 1968-1808434 | 19681112 |
| BE 723386 | A | 19690505 | BE 1968-723386 | 19681105 |
| GB 1218995 | A | 19710113 | GB 1968-1218995 | 19681111 |
| NL 6816107 | A | 19690516 | NL 1968-16107 | 19681112 |
| FR 1593627 | A | 19700601 | FR 1968-1593627 | 19681112 |
| PRIORITY APPLN. INFO.: | | | US 1967-682623 | A 19671113 |

AB HN1(M23)nX (I) (M = P, As, or Sb, Z = R or OR, n = 3-4 were prepared by treating Ni(M23)n with an acid HX. I was used in the isomerization of 3-pentenitrile (II) to 4-pentenitrile (III). Thus, 5 ml. Et2O containing 0.75 g. Ni[P(OEt)3]4 cooled to -50°, 0.10 g. concentrated H2SO4 in 5 ml. Et2O added, the mixture stirred and heated to -20° and Et2O separated, gave 0.83 g. HN1-[P(OEt)3]4HSO4 (IV). II (8.14 g.) free of III treated with

IV at -30° and heated after 45 min. to 25° gave a mixture containing cis- and trans-II and III. Other I prepared were (M, Z, and X given): P, OEt, CF3CO2; P, OEt, CN; P, OEt, CN2Cl2; P, OC6H4Me, CN;

CN; P, OC6H4OMe-P, CN and a compound of formula [Ph2PCN2CH2Ph2]NiHAlCl4.

L3 ANSWER 23 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)
 unrecovered starting material (11% unchanged) In particular a β -substituent favors methylation. The acids and amides derived from these α,α -dimethylated nitriles are described, including the new acid (CH3)2-C:CHC(CH3)2COOH, b14 118.5-19.3, m. 20-5°.

L3 ANSWER 23 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1965:480139 CAPLUS
 DOCUMENT NUMBER: 63:80139
 ORIGINAL REFERENCE NO.: 63:14696h, 14697a-e
 TITLE: Ethylenic nitriles. III. Dimethylation of ethylenic nitriles. I
 AUTHOR(S): Fleury, Jean Pierre; Bader, Andre
 SOURCE: Bulletin de la Societe Chimique de France (1965), (4), 951-7
 CODEN: BSCFAS; ISSN: 0037-8968

DOCUMENT TYPE: Journal
 LANGUAGE: French
 GI For diagram(s), see printed CA issue.
 AB cf. CA 59, 6253a. α,α -Dimethyl β,γ -ethylenic nitriles seemed suitable compds. on which to study the mechanism of acid hydrolysis. Then 3-methyl-2(or 3)-butene-, 4-methyl-3-pentene-, 3-methyl-2-pentene- and 3,4-dimethyl-3-pentenitriles treated with NaNH2 and MeI in liquid NH3 lead to the α,α -di-Me derivs. accompanied by γ -methylated products and polymers. Na (2 moles) with 0.5 g. Fe(NO3)3 are added to 1.5l. liquid NH3 to form NaNH2. Nitrile (1 mole) is added followed by slow addition of MeI. After over-night evaporation of NH3 the residue is neutralized and extracted with ether. The dried extract is distilled in vacuo to give a mixture devoid of polymer. The mixture is then fractionated using a Buechi spinning band semimicro column (30 theoretical plates) and receiving 1 g. product per hr. (reflux ratio 60:1). The nitriles used and the results of their methylation are summarized in the table. It is concluded that the methylation of α,β or β,γ ethylenic nitriles proceeds through the mesomeric carbanion (VI). The α -position is favored but considerable proportions of γ derivs. are formed, particularly on dimethylation. The structure of starting nitrile and speed of isomerization (α,β -nitrile .dblarw. β,γ -nitrile) have a large influence on the competition between polymerization and methylation. Starting material, Products, Position of methylation, % yield, S.p./mm., n20D: CH2CH:CHCN, unidentified, -, <1, -, -: CH2:CHCH2CN, unidentified, -, <1, -, -: Me2CHCH:CHCN, (CH3)2C:C(CH3)2CN (I), α , α , traces, -, -: Me2C:CHCH2CN, I, α , α , 34, 58.6-8.7°/12, 1.4330; Me2C:CHCN, CH2:C(CH3)C(CH3)2CN (II), α , α , 40, 51.3-1.5°/19.51, 1.4233; (CH3)2C:C(CH3)CN, α , 2/ or, CH3CH2C:C(CH3)2CN (III), α , α , γ , 2, 63.4-3.7°/5.5, 1.4326; CH3CH:C(CH3)C(CH3)2CN (cis + trans) (IV), α , α , γ , 4, 68.9-9.3°/15, 1.4412-5; CH:CCH3CH2CN, CH3CH2C(CH2CH3):C(CH3)CN (V), α , γ , γ : EtMeC:CHCN, III, α , α , 9; + position, IV, α , α , 31; V, α , γ , .apprx.2; isomers, + tri-Me derivs., α , α , γ and α , α , γ : (CH3)2C:MeCH2CN, α , α , 38, 64.4-4.8°/12, 1.4310; + position, Me2CHC:(CH2)CMe2CN, α , 10, -, -: Me2C:(CHCH3)CMe2CN, α , α , γ , 10, -, -: isomers, MeC:CEtCMe2CN, α , α , γ : Me2C:MeCN, II, α , 83(a); III, α , γ , 1(a); IV, α , γ , 5(a); V, γ , γ : (a) Based on

L3 ANSWER 24 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 1965:403122 CAPLUS
 DOCUMENT NUMBER: 63:3122
 ORIGINAL REFERENCE NO.: 63:532h, 533a-b
 TITLE: Thermal rearrangement of esters of cyanohydrins of α,β -unsaturated aldehydes
 AUTHOR(S): Holm, Toril
 CORPORATE SOURCE: Tech. Univ., Copenhagen
 SOURCE: Acta. Chem. Scand. (1965), 19(1), 242-5
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 63:3122

AB Thermal treatment of cyanohydrin benzoates of acrolein, crotonaldehyde, and cinnamaldehyde showed a rearrangement at about 250°, 200-300°, and 240°, resp. Ir spectra of cyanohydrin esters showed a totally quenched C=O bond. N absorption and a band at 2220-40 cm.-1. Thus, 1 mol unsatd. aldehyde and 1 mol BzCl in 200 mL. C6H6 was kept at -10° while a solution of 1.3 mol NaCN in 340 mL. H2O was added over 2 h., and the mixture stirred 2 h. at -10° and 1 h. at 20° to give cyanohydrin benzoates of the following aldehydes (% yield and phys. properties given): acrolein, 45, b0.8 115°, n25D 1.5192; crotonaldehyde, 94, b1 125°, m. 32°, cinnamaldehyde, 80, b0.5 180°, m. 69-71°. Under N a continuous stream of 35 g. acrolein cyanohydrin benzoate was led over 2 h. through a 8 mm. x 400 mm. pyrex glass tube at 520° to yield 5.5 g. trans- γ -benzoyloxycrotononitrile, m. 45-6°, and 1 g. the cis isomer, m. 32-4°, b0.7 135-7°. Crotonaldehyde cyanohydrin benzoate (120 g.) heated 5 min. at 295° gave 92:8 trans-cis mixture, b0.65 135°, n25D 1.5268, and 70:30 cis-trans mixture, b0.65 132°, n25D 1.5248, of γ -methyl- γ -benzoyloxycrotononitrile. Cinnamaldehyde cyanohydrin benzoate (40 g.) was heated 40 min. at 240°/12 mm. to give 32 g. trans- γ -phenyl- γ -benzoyloxycrotononitrile, m. 63-4°.

L3 ANSWER 25 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1962:24786 CAPLUS
 DOCUMENT NUMBER: 56:24786
 ORIGINAL REFERENCE, NO.: 56:4633b-1, 4634a-c
 TITLE: Investigations in the vitamin A series. IV. Some cases of abnormal decarboxylation

AUTHOR(S): Smit, A.
 CORPORATE SOURCE: N. V. Philips-Duphar, Weesp, Neth.
 SOURCE: Recueil des Travaux Chimiques des Pays-Bas (1961), 80, 891-904
 CODEN: RTCPA3; ISSN: 0165-0513

DOCUMENT TYPE: Journal
 LANGUAGE: English

GI For diagram(s), see printed CA Issue.

AB cf. CA 51, 298c.-The decarboxylation of cyanoionylideneacetic acid and other cyano-carboxylic acids was studied. β -Ionone (48 g.), 30 g. cyanoacetic acid, and 5 g. NH_4OAc was refluxed in 300 ml. C_6H_6 and 200 ml. HOAc 4 hrs. with removal of H_2O , the mixture cooled diluted with Et_2O , the

acids extracted with 500 ml. N NaOH , the alkaline extract washed, acidified, and the aqueous solution extracted with Et_2O to give after crystallization from C_6H_6 18 g.

trans-cyano- β -ionylideneacetic acid (II), m. 172-4, λ 272.346 μ (n 8400, 17,000); NH_4 salt m. 145-8°. The C_6H_6 mother liquors were diluted with 200 ml. petr. ether and treated with

NH_3 to give NH_4 salt of the cis acid (III), m. 158-60°. II was treated with 2N H_2SO_4 to give cis-cyano- β -ionylideneacetaldehyde acid (III), m. 122-4°, λ 274, 351 μ (n 7800, 18,700).

Similarly prepared were (starting material, product, m.p., λ , c given): α -ionone, cyano- α -ionylideneacetic acid (IV) (one isomer only), 125-7°, 282 μ , 23,700; vitamin A (mixture of trans and cis C18 ketone), 2-cyano-vitamin A acid (V), 188-93°, 399 μ , 40,600; benzalacetone, 2-carboxy-3-methyl-5-phenylpenta-2,4-dienonitrile (VI), 206-7° (decomposition), 238 and 337 μ , 10,200 and 33,300. Also prepared was citrylideneacetic acid (VII), m. 118-20°, λ 302 μ (n 26,000).

trans- β -ionylideneacetaldehyde was condensed with cyanoacetic acid in EtOH and aqueous NaOH to give cyano(β -ionylideneethylidene)acetic acid (VIII), m. 220-1°, λ 378 μ , (n 29,500).

Ionolacetic acid (36 g.) was treated with 36 ml. Ac_2O to give β -ionylidenemethane, b.p. 60-5°, λ 227, 264 μ , (n 12,300, 11,300). MeMgI was added to benzalacetone and the product dehydrated with p-toluenesulfonic acid in boiling C_6H_6 to give 2-methyl-4-phenyl-1,3-butadiene, m. 37°, λ 280 μ (n 28,200). The α -carboxy nitriles were refluxed in $\text{C}_5\text{H}_5\text{N}$ 5 parts under N , the mixture cooled, 2N H_2SO_4 added, the product extracted

with Et_2O , and purified by filtration through silica gel (not on Al_2O_3) or by distillation in vacuo to give a β , λ -unsatd. isomer of the normal α , β -unsatd. nitrile (starting material, product, b.p., λ yield, λ , E_1 given): I, C1521HN (IX), b.p. 92-5°, 85, 226 and 263 μ , 518 and 475; III, IX, b.p. 87-91°, 92, 226 and 262

L3 ANSWER 25 OF 25 CAPLUS COPYRIGHT 2007 ACS on STN (Continued)

μ , 564 and 494; IV, IX, -, 54, 234 μ , 951; V, C20H27N, -, (unstable), 319 μ , 720; VI, C12H11N, -, 86,282 μ , 1110; VII, C12H17N, -, 89, 235 μ , 876; VIII, C17H23N, -, 32, 220-3.50 μ , 300. The nitriles obtained by decarboxylation were isomerized to the α , β -unsatd. compds. by treating 1 g. nitrile with 20 ml. 2N methanolic KOH overnight at room temp. then partial purification (product,

λ yield, λ , E_1 given): β -ionylideneacetonitrile (XI), 90, 253 and 305 μ , 495 and 515; α -ionylideneacetonitrile, 95, 262 μ , 870 (after purification m. 74-5°, λ 262 μ (n 26,000)); citrylideneacetonitrile, 87, 273 μ , 825; (β -ionylideneethylidene)acetonitrile, 65, 325 μ , 752; vitamin A acid nitrile, 78, 351 μ , 1380; 3-methyl-5-phenyl-2,4-pentadienonitrile, 85, 230 and 304 μ , 592 and 1440. Crude IX chromatographed on Al_2O_3 gave X. Crude X (115 g.) was distd. in vacuo then crystd. from petr. ether to give trans- β -ionylideneacetonitrile (XI), m. 34-2-6°, λ 253, 305 μ (n 13,900, 16,600). The cis isomer could not be crystd. from X, so it was prepd. from cis- β -ionylideneacetic (XII). Treatment of XII with PCl_3 followed by NH_3 gave 38% cis- β -ionylideneacetamide (XIII), m. 132-4°, λ 250, 299 μ , (n 11,000, 13,200). The trans amide was prepd. similarly (48% yield), m. 121-2°, λ 254, 299 μ (n 13,800, 15,600). XIII (10 g.) in 30 ml. C_6H_6 and 8.7 g. Et_3N was treated with 8.1 g. P_2O_5 at 0° then heated 1 hr. at 80° to give 6.1 g. XIII and 1.1 g. cis- β -ionylideneacetonitrile, m. 35.8-6.0°, mixed m.p. with XI below 18°, λ 250, 305 μ (n 10,500, 13,200). Degradation of IX by ozonolysis gave 30.2-32.8% geronic acid semicarbazone, compared with 25.8-30.8% on ozonolysis of XI and 28.6%-30.9% on ozonolysis of β -ionone. Several possibilities for the structure of IX were eliminated on the basis of the ozonolysis and spectral data, leaving the β -methylene structure. In the case of the decarboxylation of VII and VIII, the structure of the new product was considered to be that with a β , γ -double bond conjugated with a δ -methylene group, on the basis of comparison of the spectra with those of known compounds of analogous structure. On KOH treatment, the double bonds rearranged to the expected α , γ , δ -conjugated compd. The authors concluded that the isomerization took place after the decarboxylation, rather than before, as was the case in other decarboxylation reactions.

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